

PATENT SPECIFICATION

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(54) STABILIZED PIGMENTED POLYCARBONATE COMPOSITION

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1, River Road, Schenectady, 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

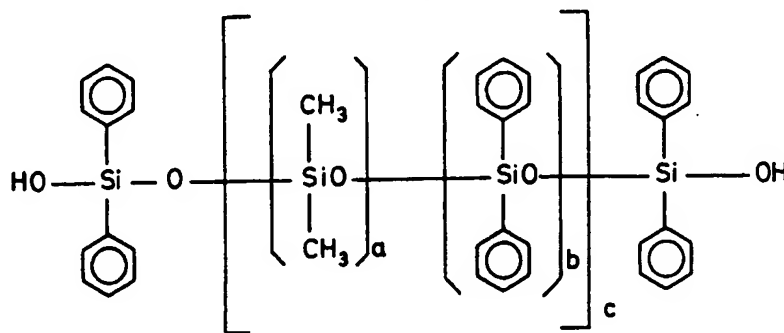
This invention is directed to a stabilized pigmented polycarbonate composition comprising a mixture of an aromatic carbonate polymer with a pigment and a stabilizing amount of a silanol. The composition may additionally contain a phosphite and/or an epoxy compound.

In the past, much effort has been expended in preparing thermally stable polycarbonate compositions which would be color stable at elevated temperatures and particularly at the high molding temperatures generally employed to prepare molded polycarbonate articles. Many different additives have been found that are quite suitable for rendering polycarbonates heat and color stable. Particularly useful are triorgano-phosphites which have been disclosed in U.S. Patent No. 3,305,520. Also, U.S. Patent No. 3,729,440 discloses a thermally stable aromatic polycarbonate containing a phosphinite and an epoxy compound. Further, U.S. Patent No. 3,673,146 discloses a method for stabilizing polycarbonate resin involving using a triorganophosphite, cycloaliphatic epoxy compound, ultramarine pigment and aryl siloxane fluid.

For many commercial applications, it is necessary to add a pigment or colorant to the basic polymer formulations to enhance their appearance. Metal oxides such as, for example, titanium dioxide and zinc oxide have become universal pigments because of their stability and high opacity. In addition, they have excellent resistance to light, heat, acid, alkalies, and generally, to oxidation and reduction. Furthermore, they may be used in conjunction with other pigments and dyes to provide polymeric formulations having a wide variety of colors. There is, however, one very serious limitation on the use of metal oxides in polycarbonate compositions. It has been found that many of the physical properties of polycarbonates are substantially reduced when metal oxides are added. As a result, the pigment content must be maintained at a low level when a strong, tough plastic material is required, limiting the variety and intensity of colors producible.

It has been discovered that when a pigmented aromatic carbonate polymer is mixed with a stabilizing amount of a silanol, the resulting polycarbonate composition has improved thermal, color and melt stability as compared with aromatic carbonate polymers containing either organic phosphites or mixtures of organic phosphites and epoxy compounds. Additionally, the composition according to the invention may contain co-stabilizing amounts of a phosphite and/or an epoxy compound.

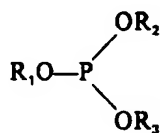
The present invention provides a stabilized polycarbonate composition which comprises a mixture of an aromatic carbonate polymer, and, based on the weight of the composition, 0.0001 to 10.0 weight percent of a metal oxide pigment, and 0.01 to 1.0 weight percent, of a silanol of the general formula



wherein *a*, *b*, and *c* are each from 1 to 100.

The silanols used according to the present invention are prepared by methods known in the art such as those described in U.S. Patent No. 2,854,242; British Patent No. 935,709 and German Patent No. 1,198,068.

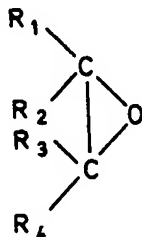
The co-stabilizing organophosphites which can be employed herein are of the formula:



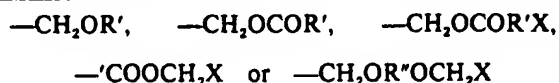
wherein *R*₁, *R*₂ and *R*₃ are independently hydrogen, alkyl, aryl, cycloalkyl, aralkyl or alkylaryl radicals wherein at least one *R* is other than hydrogen. Preferably the radicals have 1 to 20 carbon atoms. The alkyl may be methyl, ethyl, propyl, isopropyl, the various butyl isomers, e.g., butyl, sec-butyl, tert-butyl, the various amyl isomers, the various hexyl isomers, the various nonyl isomers, or the various cicosyl isomers; the cycloalkyl may be cyclobutyl, cyclohexyl, 2-methylcyclohexyl, 4-methylcyclohexyl, 2-ethylcyclohexyl, 4-ethylcyclohexyl, or 4-isopropylcyclohexyl, the aryl may be phenyl, 1-naphthyl, 2-naphthyl, biphenyl or terphenyl, the aralkyl may be any of the above alkyl, substituted with one or more of the above aryl groups, e.g., benzyl, phenylethyl or 1-phenylpropyl; and the alkaryl may be any of the above aryls substituted with one or more of the above alkyls, e.g., *o*-tolyl, xylyl, cumyl, mesityl, butylphenyl, or nonylphenyl. Typical of some of the phosphites that can be employed in the practice of this invention are diphenyl dodecyl phosphite, triphenylphosphite, di-(*t*-butylphenyl)octyl phosphite, tris(nonylphenyl) phosphite, and dipropylphenyl phosphite. The preferred phosphites to be employed herein are trialkyl phosphites, e.g., tris(*p*-nonylphenyl) phosphite or tridecylphosphite or diaryl alkyl phosphites, e.g., diphenyldecylphosphite. The phosphite is preferably present in an amount of from 0.005 to 1.0 weight percent and more particularly 0.01 to 0.2 weight percent based on the weight of the polycarbonate composition.

The co-stabilizing epoxy compounds are selected from the following:

I. Derivatives of epoxy ethane represented by the following formula

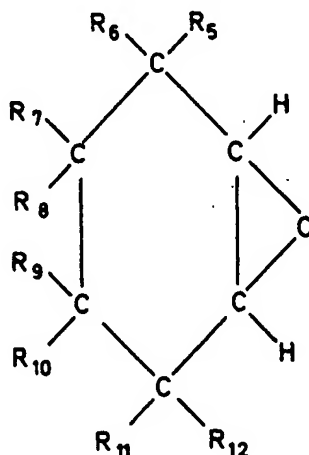


wherein *R*₁, *R*₂, *R*₃ and *R*₄ are independently hydrogen, alkyl of 1—24 carbon atoms, aryl radical of 6—24 carbon atoms,

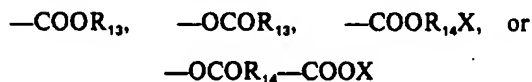


wherein R' is alkyl of 1—24 carbon atoms or aryl of 6 to 24 carbon atoms, R'' is alkylene or 1—24 carbon atoms and X is an oxirane ring.

5 II. Derivatives of epoxy cyclohexane represented by the following formula: 5



wherein R₅ to R₁₂ are each hydrogen, alkyl of 1—24 carbon atoms,



10 wherein R₁₃ is alkyl of 1—24 carbon atoms and R₁₄ is alkylene of 1—24 carbon atoms and X is an oxirane ring. 10

While the actual number of hydrogen atoms employed may vary it should be a function of the volatility of the epoxy compound. The number of hydrogen atoms should be such as to minimize the volatility of the epoxy compound, since if the epoxy compound were to volatilize at a low temperature, its benefit in use with a polycarbonate would be lost at the moulding temperatures employed in preparing molded articles from the composition of this invention.

The amount of epoxy employed in the practice of this invention is preferably from 0.01 to 0.5 weight percent, based on the weight of the polymer composition, and is most preferably 0.03 to 0.30 weight percent. While more than 0.5 weight percent of epoxy can be employed, it has been found that higher amounts tend to degrade the physical properties of the polycarbonate and thereby reduce the usefulness of the polymer in providing tough, flexible molded articles.

Epoxy compounds that have been employed in the practice of this invention, include 3,4 - epoxy - cyclohexylmethyl - 3,4 - epoxy cyclohexane carboxylate, 3,4 - epoxy - 6 - methylcyclohexylmethyl, 3,4 - epoxy - 6 - methylcyclohexane carboxylate, 2,3 - epoxycyclohexylmethyl, 3,4 - epoxycyclohexane carboxylate, 4 - (3,4 - epoxy - 5 - methylcyclohexyl) butyl - 3,4 - epoxycyclohexane carboxylate, 3,4 - epoxycyclohexyl ethyleneoxide, cyclohexyl 3,4 - epoxy - cyclohexane carboxylate, 3,4 - epoxy - 6 - methylcyclohexylmethyl - 6 - methylcyclohexyl carboxylate, bisphenol-A diglycidyl ether, tetrabromobisphenol-A diglycidyl ether, diglycidyl ester of phthalic acid, diglycidyl ester of hexahydrophthalic acid, epoxidized soybean oil, epoxidized linseed oil, bisepoxycyclohexyl adipate, butadiene diepoxide, tetraphenylethylene - epoxide, octyl epoxy tallate and epoxidized polybutadiene. Also, 3,4 - dimethyl - 1,2 - epoxycyclohexane, 3,5 - dimethyl - 1,2 - epoxy cyclohexane, 3 - methyl - 5 - tert butyl - 1,2 - epoxy cyclohexane, octadecyl 2,2 - dimethyl - 3,4 - epoxycyclohexane carb xylate, N - butyl 2,2 - dimethyl - 3,4 - epoxy cyclohexane carboxylate, cyclohexyl 2 - methyl - 3,4 - epoxycyclohexane carboxylate, N - butyl 2 - isopropyl - 3,4 - epoxy - 5 - methylcyclohexane carboxylate, octadecyl -

3,4 - epoxycyclohexane carboxylate, 2 - ethylhexyl - 3',4' - epoxycyclohexane carboxylate, 4,6 - dimethyl - 2,3 - epoxycyclohexyl - 3',4' - epoxy cyclohexane carboxylate, diethyl 4,5 - epoxy - cis - 1,2 - cyclohexane dicarboxylate, and di - n - butyl 3 - tert butyl - 4,5 - epoxy - cis - 1,2 cyclohexane dicarboxylate. Specifically, any of the epoxycyclohexyl compounds meet the general formula of II and the other epoxy compounds recited herein meet the general formula of I. Preferably, the epoxy compound employed in the practice of this invention is 3,4 - epoxycyclohexylmethyl 3,4 - epoxycyclohexane carboxylate.

The aromatic carbonate polymers employed in the practice of this invention are homopolymers and copolymers and mixtures thereof that are prepared by reacting a dihydric phenol with a carbonate precursor.

The dihydric phenols that can be employed are bisphenols such as bis(4 - hydroxyphenyl) methane, 2,2 - bis(4 - hydroxyphenyl) propane (hereinafter referred to as bisphenol-A), 2,2 - bis(4 - hydroxy - 3 - methylphenyl) propane, 4,4 - bis(4 - hydroxyphenyl) heptane, 2,2 - bis(4 - hydroxy - 3,5 - dichlorophenyl) propane, and 2,2 - bis(4 - hydroxy - 3,5 - dibromophenyl) propane; dihydric phenol ethers such as bis(4 - hydroxyphenyl) ether, and bis(3,5 - dichloro - 4 - hydroxyphenyl) ether; dihydroxydiphenyls such as *p,p'* - dihydroxydiphenyl and 3,3' - dichloro - 4,4 - dihydroxydiphenyl; dihydroxyaryl sulfones such as bis(4 - hydroxyphenyl) sulfone, and bis(3,5 - dimethyl - 4 - hydroxyphenyl) sulfone; dihydroxy benzenes, resorcinol, hydroquinone, halo- and alkyl - substituted dihydroxy benzenes such as 1,4 - dihydroxy - 2,5 - dichlorobenzene, and 1,4 - dihydroxy - 3 - methylbenzene; and dihydroxydiphenyl sulfoxides such as bis(4 - hydroxyphenyl) sulfoxide, and bis(3,5 - dibromo - 4 - hydroxyphenyl) sulfoxide. A variety of additional dihydric phenols are also available to provide carbonate polymers and are disclosed in U.S. Patents No. 2,999,835, 3,028,365 and 3,153,008. Also suitable are copolymers prepared from any of the above copolymerized with halogen-containing dihydric phenols such as 2,2 - bis(3,5 - dichloro - 4 - hydroxyphenyl) propane and 2,2 - bis(3,5 - dibromo - 4 - hydroxyphenyl) propane. It is, of course, possible to employ two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with hydroxy or acid terminated polyester, or with a dibasic acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the compositions of this invention. Also employed in the practice of this invention may be blends of any of the above materials to provide the aromatic carbonate polymer.

The carbonate precursor may be either a carbonyl halide, a carbonate ester or a haloformate. The carbonyl halides which can be employed herein are carbonyl bromide, carbonyl chloride and mixtures thereof. Typical of the carbonate esters which may be employed herein are diphenyl carbonate, di - (halophenyl) carbonates such as di(chlorophenyl carbonate, di - bromophenyl) carbonate, di - (trichlorophenyl) carbonate, or di - (tribromophenyl) carbonate; di - (alkylphenyl) carbonate such as di(tolyl) carbonate; di - (naphthyl) carbonate, di - (chloronaphthyl) carbonate, phenyl tolyl carbonate, chlorophenyl chloronaphthyl carbonate, or mixtures thereof. The haloformates suitable for use herein include bis - haloformates of dihydric phenols (bischloroformates of hydroquinone) or glycols (bishaloformates of ethylene glycol, neopentyl glycol, or polyethylene glycol). While other carbonate precursors will occur to those skilled in the art, carbonyl chloride, also known as phosgene, is preferred.

Also included are the polymeric derivatives of a dihydric phenol, a dicarboxylic acid and carbonic acid. These are disclosed in U.S. Patent No. 3,169,121.

The aromatic carbonate polymers used in the compositions of this invention are prepared by employing a molecular weight regulator, an acid acceptor and a catalyst. The molecular weight regulators which can be employed include monohydric phenols such as phenol, chroman-I, paratertiarybutylphenol, parabromophenol, primary and secondary amines. Preferably, phenol is employed as the molecular weight regulator.

A suitable acid acceptor may be either an organic or an inorganic acid acceptor. A suitable organic acid acceptor is a tertiary amine and includes such materials as pyridine, triethylamine, dimethylaniline, or tributylamine. The inorganic acid acceptor may be one which can be either a hydroxide, a carbonate, a bicarbonate, or a phosphate of an alkali or alkaline earth metal.

The catalysts which are employed herein can be any of the suitable catalysts that aid the polymerization of bisphenol-A with phosgene. Suitable catalysts include tertiary amines for example, triethylamine, tripropylamine, or N,N -

dimethylaniline; quaternary ammonium compounds for example, tetraethylammonium bromide, cetyl triethylammonium bromide, tetra - n - heptylammonium iodide, tetra - n - propylammonium bromide, tetramethylammonium chloride, tetramethylammonium hydroxide, tetra - n - butylammonium iodide, or benzyltrimethylammonium chloride; and quaternary phosphonium compounds for example, n - butyl - triphenyl phosphonium bromide and methyltriphenyl phosphonium bromide.

Also, included herein are branched polycarbonates wherein a polyfunctional aromatic compound is reacted with the dihydric phenol and carbonate precursor to provide a thermoplastic randomly branched polycarbonate.

These polyfunctional aromatic compounds contain at least three functional groups which are carboxyl, carboxylic anhydride, haloformyl or mixtures thereof. Examples of these polyfunctional aromatic compounds include: trimellitic anhydride, trimellitic acid, trimellityl trichloride, 4 - chloroformyl phthalic anhydride; pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, benzophenonetetracarboxylic acid, and benzophenonetetracarboxylic anhydride. The preferred polyfunctional aromatic compounds are trimellitic anhydride or trimellitic acid, or their haloformyl derivatives.

Also included herein are blends of a linear polycarbonate and a branched polycarbonate.

The aromatic carbonate polymers are mixed with those pigments known in the art that are able to withstand a temperature of at least 200°F are suitable for purposes of the present invention. The pigment should preferably be in the form of a finely divided powder to ensure complete dispersion in the polycarbonate. Preferred pigments include titanium dioxide, zinc oxide, lead oxide, iron oxide and chrome oxide.

The pigments are used in amounts of from 0.0001 to 10.0 weight percent based on the weight of the polycarbonate composition.

The silanol as well as the phosphite and epoxy additive may be mixed with aromatic carbonate polymers by any one of a variety of methods commonly employed for incorporation of additive. Additionally, in the case of pigments such as titanium dioxide, for example, the pigment may be coated with the silanol and then added to the aromatic carbonate polymer.

Obviously, other materials can also be employed with the aromatic carbonate polymer compositions of this invention and include such materials as antistatic agents, mold release agents, thermal stabilizers, ultraviolet light stabilizers, reinforcing fillers such as glass and other inert fillers, and foaming agents.

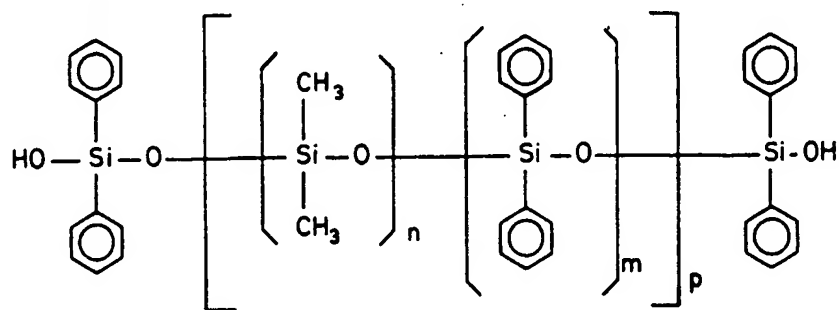
The following examples are set forth to illustrate this invention more clearly. Unless otherwise specified, where parts or percents are mentioned, they are parts or percents by weight.

(REFERENCE) EXAMPLE I

A polycarbonate composition of a homopolymer of 2,2 - bis(4 - hydroxyphenyl) propane (hereinafter referred to as bisphenol-A) prepared by reacting essentially equimolar amounts of bisphenol-A and phosgene in an aqueous organic medium with triethylamine, sodium hydroxide, and phenol, under standard conditions is mixed with 2.0 weight percent of titanium dioxide and 0.1 weight percent trisnonylphenylphosphite. This composition is then fed to an extruder which extruder is operated at about 550°F, and the extrudate strands are chopped into pellets. The pellets are injection molded into test samples of about 3 inches by 2 inches by 1/8 inch thick at 600°F and 680°F. The composition is designated as Sample A. Thermal stability to discoloration is measured in accordance with ASTM Yellowness Index Test D1925 on samples molded at 600°F and 680°F. These results are set forth in Table I.

EXAMPLE II

Example I is repeated except that 0.05 weight percent of a silanol of the following formula:



wherein $n=1.8$; $m=2.2$; and $p=1$, is added to the composition of Example I. This composition is designated Sample B. The pellets produced from this composition are injection molded and subjected to the test as described in Example I. The results are tabulated in Table I.

EXAMPLE III

Example II is repeated except that 0.09 weight percent of the silanol is employed in place of the 0.06 weight percent of silanol. This composition is designated Sample C. The pellets produced from this composition are injection molded and subjected to the test as described in Example I. The results are tabulated in Table I.

EXAMPLE IV

Example II is repeated except that 0.15 weight percent of the silanol is employed in place of the 0.06 weight percent of silanol. This composition is designated Sample D. The pellets produced from this composition are injection molded and subjected to the test as described in Example I. The results are tabulated in Table I.

EXAMPLE V

Example II is repeated except that 0.20 weight percent of the silanol is employed in place of the 0.06 weight percent of silanol. This composition is designated Sample E. The pellets produced from this composition are injection molded and subjected to the test as described in Example I. The results are tabulated in Table I.

TABLE I

Yellowness Index
as Molded at

Sample	600°F	680°F
A	7.9	9.7
B	6.9	8.3
C	6.7	7.5
D	6.7	7.9
E	6.4	7.1

As regards the data in Table I, the lower the Yellowness Index number, the lower is the discoloration of the polymer and, therefore, the better is the thermal stability of the polymer.

(REFERENCE) EXAMPLE VI

A polycarbonate composition of a homopolymer of 2,2 - bis(4 - hydroxyphenyl) propane (hereinafter referred to as bisphenol-A) prepared by reacting essentially equimolar amounts of bisphenol-A and phosgene in an aqueous organic medium with triethylamine, sodium hydroxide, and phenol, under standard conditions. The composition is then fed to an extruder, which extruder is operated at about 550°F and the extrudate strands are chopped into pellets. These pellets are then fed into a Gottfert capillary rehometer which is heated to 300°C. The melt viscosity is measured after 7 minutes and 40 minutes. This composition is designated Sample F. The percent change in melt viscosity between the 40 minute reading and the 7 minute reading is set forth in Table II.

(REFERENCE) EXAMPLE VII

Example VI is repeated except that 2.0 weight percent of titanium dioxide is added to the composition of Example VI. This composition is designated Sample G. The pellets produced from this composition are subjected to the test as described in Example VI. The results are tabulated in Table II.

(REFERENCE) EXAMPLE VIII

Example VII is repeated except that 0.10 weight percent of trisn-octylphenylphosphite is added to the composition of Example VII. The composition is designated Sample H. The pellets produced from this composition are subjected to the test as described in Example VI. The results are tabulated in Table II.

EXAMPLE IX

Example VIII is repeated except that 0.30 weight percent of the silanol of Example II is added to the composition of Example VIII. The composition is designated Sample I. The pellets produced from this composition are subjected to the test as described in Example VI. The results are tabulated in Table II.

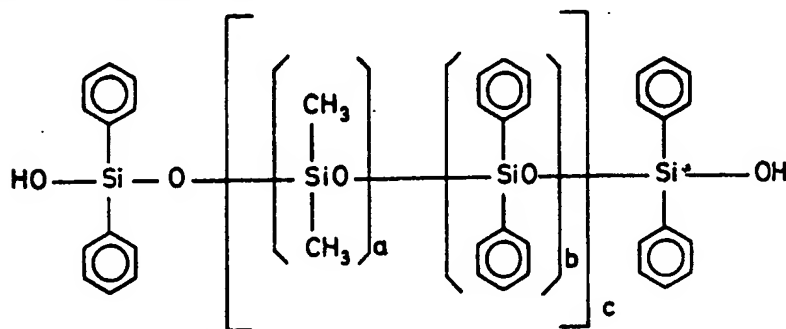
TABLE II
Percent change in
Melt Viscosity at
7/40 minutes

Sample	
F	-1.1
G	-59.5
H	-27.8
I	-12.5

The data in Table II shows that pigment added to a polycarbonate composition results in reduction of melt viscosity of Sample G. When a stabilizer is added, the melt viscosity is not reduced to such a large extent as with pigment alone. When a silanol is added in addition to the stabilizer of Sample H, the designation is reduced.

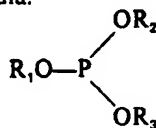
WHAT WE CLAIM IS:—

1. A stabilized polycarbonate composition which comprises a mixture of an aromatic carbonate polymer, and, based on the weight of the composition, 0.0001 to 10.0 weight percent of a metal oxide pigment, and 0.01 to 1.0 weight percent, of a silanol of the general formula,



wherein *a*, *b*, and *c* are each from 1 to 100.

2. A composition as claimed in Claim 1 which contains a stabilizing amount of an organophosphite of the formula:



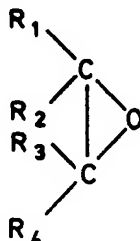
wherein *R*₁, *R*₂ and *R*₃ are independently hydrogen, alkyl, aryl, cycloalkyl, aralkyl or alkaryl radicals and at least one *R* is other than hydrogen.

3. A composition as claimed in Claim 2 which comprises from 0.005 to 1.0 weight percent of the organophosphite based on the composition.

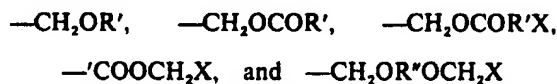
4. A composition as claimed in Claim 2 or 3 which comprises from 0.01 to 0.2 weight percent of the organ phosphite, based on the composition.

5. A composition as claimed in any preceding Claim further comprising a stabilizing amount of an epoxy compound selected from

(I) derivatives of epoxy ethane having the formula:

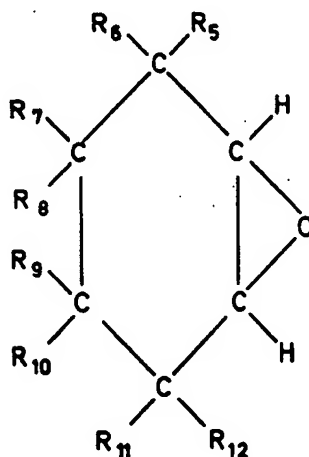


wherein R_1 , R_2 , R_3 and R_4 are independently hydrogen, alkyl of 1 to 24 carbon atoms, aryl of 6 to 24 carbon atoms,

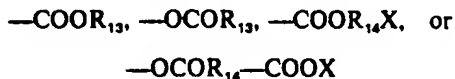


wherein R' is alkyl of 1 to 24 carbon atoms or aryl of 6 to 24 carbon atoms, R'' is alkylene of 1 to 24 carbon atoms and X is an oxirane ring, and

(II) derivatives of epoxy cyclohexane having the formula:



wherein R_5 to R_{12} are each hydrogen, alkyl of 1 to 24 carbon atoms,



wherein R_{13} is alkyl of 1 to 24 carbon atoms, and R_{14} is alkylene of 1 to 24 carbon atoms and X is an oxirane ring.

6. A composition as claimed in Claim 5 which comprises from 0.01 to 0.5 weight percent of the epoxy compound based on the composition.

7. A composition as claimed in Claim 5 or 6 which comprises from 0.03 to 0.30 weight percent of the epoxy compound, based on the composition.

8. A composition as claimed in any preceding Claim wherein the pigment is titanium dioxide.

9. A composition as claimed in Claim 1 and substantially as hereinbefore described with reference to any of Examples II to V and IX.

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